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(54) Title: OVERBASED ALKYL OXY BENZENE SULFONATES AS DETERGENTS (57) Abstract A marine lubricating oil has a major amount of oil of lubricating viscosity; and a minor amount of an overbased, alkyl oxy benzene sulfonate having a TBN of at least 200. Between 40 wt.% and 80 wt.% of the alkyl group is attached at the 4-position and higher positions of the alkyl group. The oxy group can be hydroxy, methoxy, ethoxy, propoxy, butoxy, pentoxy, or hexoxy.		

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OVERBASED ALKYL OXY BENZENE SULFONATES AS DETERGENTS

5 The present invention relates to an additive especially useful in a marine lubricating oil.

BACKGROUND OF THE INVENTION

10 U.S. 3,523,898 teaches that overbased alkyl phenol sulfonic acids are useful as detergents in lubricating oils. The alkyl groups appear to be attached at either the 1- or 2- position of the alkyl groups, and the TBN appears to limited to 150 or less.

15 British 1,372,532 teaches that mixtures of overbased, alkyl hydroxy benzene sulfonates and alkylsalicylic acids are useful in lubricating oils. The alkyl groups of the sulfonates appear to be attached at either the 1- or 2- position of the alkyl groups. The TBN appears to be about 200.

20 British 1,332,473 teaches that overbased, alkyl hydroxy benzene sulfonates are useful as an oil-soluble dispersant in lubricating oils. The patent is silent as to where the alkyl groups are attached. The TBN appears to be about 400, with a very high base ratio.

25 U.S. 4,751,010 teaches that partial sulfonation of alkylphenol results in the formation of an alkyl hydroxy benzene sulfonate that can be overbased using sulfurization and carbonation. The patent is silent as to where the alkyl groups are attached. The TBN appears to be in the range of from 200 to 250.

30 U.S. 5,330,663 and 5,330,664 teach overbased alkylphenoxy sulfonates that have alkyl groups derived from substantially straight-chained olefins that are either internal or alpha. It does not teach using olefins that are partially internal olefins.

35 U.S. Patent Nos. 3,523,898; 4,751,010; 5,330,663; and 5,330,664 are all hereby incorporated by reference for all purposes.

SUMMARY OF THE INVENTION

The present invention provides a lubricating oil having a major amount of base oil of lubricating viscosity; and a minor amount of an overbased, alkyl oxy benzene sulfonate having a TBN of at least 200, preferably at least 250, between 40 wt. % and 80 wt. % of the alkyl group is attached at the 4- position and higher positions of the alkyl group. Preferably, between 45 wt. % and 70 wt. % of the alkyl group is attached at the 4- position and higher positions of the alkyl group. This lubricating oil is especially useful as a marine lubricating oil.

The oxy group can be either hydroxy, methoxy, ethoxy, propoxy, butoxy, pentoxy, or hexoxy. Preferably, it is hydroxy.

Preferably, the alkyl group of the overbased, alkyl oxy benzene sulfonate has from eighteen to thirty carbon atoms per alkyl group. More preferably, it has from twenty to twenty-four carbon atoms per alkyl group.

One process for making this overbased, alkyl oxy benzene sulfonate comprises alkylating an oxy benzene with an olefin between 40 wt. % and 80 wt. % internal olefins to produce an alkyl oxy benzene, then sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid; and overbasing the alkyl oxy benzene sulfonic acid to produce the overbased, alkyl oxy benzene sulfonate. Preferably, the internal olefin is produced by isomerizing an olefin using an iron pentacarbonyl catalyst.

In an alternative embodiment of the present invention, an additive is produced by alkylating an oxy benzene with a polyalpha olefin having an activity of at least 80% to produce an alkyl oxy benzene, sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid, and overbasing the alkyl oxy benzene sulfonic acid to produce an overbased, alkyl oxy benzene sulfonate having a TBN of at least 200, preferably at least 250.

DETAILED DESCRIPTION OF THE INVENTION

In its broadest aspect, the present invention involves highly overbased, alkyl oxy benzene sulfonate detergents where at least 40 wt. % of the alkyl groups are attached at the 4- position and higher positions of the

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alkyl group. When at least 40 wt.% of the alkyl groups are attached at the 4-position and higher position, the viscosity is lowered significantly.

On the other hand, at least 20 wt.% of the alkyl groups should be attached at the 1-, 2-, and 3- position in order to reduce high temperature deposit formation. While Applicants do not wish to be bound by any particular theory of operation, it is believed that too high of internal attachment leads to structures that are similar to materials derived from branched olefins. Such materials tend to decompose readily at the branching.

In one embodiment, between 40 wt.% and 80 wt. % (preferably between 45 wt.% and 70 wt. %) of the alkyl group is attached at the 4-position and higher positions of the alkyl group. This type of additive can be produced by alkylating an oxy benzene with an olefin containing between 40 wt.% and 80 wt. % internal olefins to produce an alkyl oxy benzene, sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid; and overbasing the alkyl oxy benzene sulfonic acid to produce the overbased, alkyl oxy benzene sulfonate. An olefin containing between 20 wt.% and 60 wt. % internal olefins can be formed by isomerizing an alpha olefin using an iron pentacarbonyl catalyst.

In another embodiment, the additive is produced by alkylating an oxy benzene with a polyalpha olefin having an activity of at least 80% to produce an alkyl oxy benzene, sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid; and overbasing the alkyl oxy benzene sulfonic acid to produce an overbased, alkyl oxy benzene sulfonate having a TBN of at least 250.

The present invention comes out of work in trying to find an inexpensive alternative to the use of salicylates in lube oils for marine applications. That alternative should have a TBN of over 250, have a viscosity of less than 600 cSt, and have comparative properties with commercial salicylates.

The initial attempts were with an overbased oxy benzene sulfonate having a linear C₂₀-C₂₈ alkyl group. That material turned out to be so viscous

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that its viscosity could not be measured. It was so viscous that it didn't flow from a beaker even when left overturned for over a weekend.

We overcame this problem by using an overbased alkyl oxy benzene sulfonate having alkyl groups that were isomerized prior to alkylation of the benzene. It is essential that alkyl groups of the overbased alkyl oxy benzene sulfonate be predominately attached at the 4- position and higher positions of the alkyl group.

10 THE OVERBASED ALKYL OXY BENZENE SULFONATE

The lubricating oil has a minor amount of an overbased, alkyl oxy benzene sulfonate having a TBN of at least 200, preferably at least 250, wherein at least 40 wt. % of the alkyl group of the sulfonate is attached at the 4- position and higher positions of the alkyl group. The oxy group can be either hydroxy, methoxy, ethoxy, propoxy, butoxy, pentoxy, or hexoxy. Preferably, it is hydroxy.

By "TBN," we mean "Total Base Number," which refers to the amount of base equivalent to one milligram of KOH in one gram of additive. Thus, higher TBN numbers reflect more alkaline products and therefore a greater alkalinity reserve. The Total Base Number for an additive composition is readily determined by ASTM test method D664 or other equivalent methods.

By "internal olefins," we mean an olefin wherein the double bond is at the 4- position and higher positions of the alkene, instead of at the 1-, 2-, or 3- position.

Preferably, the alkyl group of the overbased, alkyl oxy benzene sulfonate has from eighteen to thirty carbon atoms per alkyl group. More preferably, the alkyl group has from twenty to twenty-four carbon atoms per alkyl group.

The additive of the present invention can be produced by alkylating an oxy benzene with an olefin containing between 40 wt. % and 80 wt. % internal olefins to produce an alkyl oxy benzene, sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid; and overbasing the alkyl oxy

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benzene sulfonic acid to produce the overbased, alkyl oxy benzene sulfonate. An olefin containing between 40 wt. % and 80 wt. % internal olefins can be formed by isomerizing an alpha olefin using an iron pentacarbonyl catalyst.

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The processes of alkylating an alkyl oxy benzene with an olefin to produce an alkyl oxy benzene, and sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid are both discussed in detail in U.S. Patent Nos. 5,330,663 and 5,330,664, which have been incorporated by reference for all purposes. Our alkylation and sulfonation processes differ only in the olefins used and reaction time. In our batch alkylation reaction, we need only about six to eight hours. The preferred sulfonation process is a falling film process using a charge mole ratio of sulfur trioxide to alkylphenol of 1.1:1 and a reaction temperature in the range of from 70° to 100° C, followed by immediate neutralization.

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A neutralized slurry of alkyl oxy benzene sulfonic acid is added to a slurry of xylenes, methanol, and calcium hydroxide. The resulting slurry is then carbonated during which a second slurry of alkyl oxy benzene sulfonic acid and a second slurry of xylenes, methanol, and calcium hydroxide are added. After the carbonation, the material is stripped to remove methanol and water. Lube oil is then added and the solids removed. The remainder of the solvents are then stripped off and additional lube oil added to adjust the product to the final base number.

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THE LUBRICATING OIL PRODUCT

The oil-soluble, highly overbased, alkyl oxy benzene sulfonate additive compositions produced by the process of this invention are useful lubricating oil additives imparting detergency and dispersency properties when added to the lubricating oil composition employed in the crank case of an internal combustion engine. Such lubricating oil compositions comprise a major amount of base oil of lubricating viscosity; and a minor amount of oil-soluble, highly overbased, alkyl oxy benzene sulfonate additive compositions. These lubricating oil compositions are useful in diesel engines, gasoline engines, as well as in marine engines.

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Such lubricating oil compositions employ a finished lubricating base oil of lubricating viscosity which may be single or multigrade. Multigrade lubricating base oils are prepared by adding viscosity index (VI) improvers. Typical viscosity index improvers are polyalkyl methacrylates, ethylene and propylene copolymers, styrene-diene copolymers, and the like.

The lubricating base oils used in such compositions may be mineral oils or synthetic oils of viscosity suitable for use in the crank case of an internal combustion engine such as gasoline engines and diesel engines which include marine engines. Crank case lubricating oils ordinarily have a viscosity of about 1300 cSt at 0° F to 24 cSt at 210° F (99° C). The lubricating base oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in the invention includes paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of α -olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C_6 to C_{12} α -olefins such as 1-decene trimer. Likewise, alkylbenzenes of proper viscosity such as didodecyl benzene, can be used. Useful synthetic esters include esters of both monocarboxylic acids and polycarboxylic acids as well as monohydroxy alkenols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaproate, di-2-ethylhexyl adipate, dilaurylsebacate and the like. Complex esters prepared from mixtures of mono and dicarboxylic acid and mono and dihydroxy alkanols can also be used,

Blends of hydrocarbon oils with synthetic oils are also useful. For example, blends of 10 to 25 wt. % hydrogenated 1-decene trimer with 75 to 90 wt. % 150 SUS (100° F) mineral oil gives an excellent lubricating base oil.

In one embodiment, the lubricating oil also has an ashless dispersant and a zinc dialkyldithiophosphate.

In another embodiment, the lubricating oil also has a detergent selected from the group consisting of metal phenates, metal sulfonates, and metal salicylates.

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Other additives which may be present in the formulation include rust inhibitors, foam inhibitors, corrosion inhibitors, metal deactivators, pour point depressants, anti-oxidants, and a variety of other well-known additives

- 5 More specifically, the following additive components examples of components that can be favorably employed in combination with the overbased, alkyl oxy benzene sulfonate of the present invention
- (1) Metallic detergents: overbased sulfurized alkylphenates, overbased sulfonates, and overbased salicylates.
 - 10 (2) Ashless dispersants: alkenyl succinimides, alkenyl succinimides modified with other organic compounds, and alkenyl succinimides modified with boric acid, alkenyl succinic ester.
 - (3) Oxidation inhibitors
 - 15 1) Phenol type phenolic) oxidation inhibitors: 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-(methylenebis(4-methyl-6-tert-butyl-phenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert- α -dimethylamino-p-cresol, 2,6-di-tert-4-(N,N' dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)-sulfide, and bis (3,5-di-tert-butyl-4-hydroxybenzyl).
 - 20 2) Diphenylamine type oxidation inhibitor: alkylated diphenylamine, phenyl- α -naphthylamine, and alkylated α -naphthylamine.
 - 30 3) Other types: metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis(dibutyldithiocarbamate).
 - (4) Rust inhibitors (Anti-rust agents)
 - 35 1) Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether,

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polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol monooleate.

- 2) Other compounds: stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.
- (5) Demulsifiers: addition product of alkylphenol and ethyleneoxide, poloxyethylene alkyl ether, and polyoxyethylene sorbitane ester.
- (6) Extreme pressure agents (EP agents): zinc dialkyldithiophosphate (Zn-DTP, primary alkyl type & secondary alkyl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, benzyl iodide, fluoroalkylpolysiloxane, and lead naphthenate.
- (7) Friction modifiers: fatty alcohol, fatty acid, amine, borated ester, and other esters
- (8) Multifunctional additives: sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphoro dithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound
- (9) Viscosity index improvers: polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.
- (10) Pour point depressants: polymethyl methacrylate

EXAMPLES

30 The invention will be further illustrated by following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

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COMPARATIVE EXAMPLE ALKYLATION USING NORMAL α -OLEFINS

A. Preparation of Alkylated Phenols

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High overbased alkyl hydroxy benzene sulfonates were prepared using an alkylphenol derived by contacting 3.0 moles of phenol per each mole of a normal C₂₀ to C₂₄ α -olefin mixture using Amberlyst-36 catalyst [a polystyrene cross-linked sulfonic acid resin having a Hammett acid function (H_a) of less than -2.2 and an acid number of 5.4 milliequivalents per gram].
10 Amberlyst-36 resin catalyst is commercially available from Rohm & Haas, Philadelphia, PA.

The olefin mixture had the following olefinic positions, determined by
15 using a macro program using Nuclear Magnetic Resonance Spectroscopy (NMR).

	<u>wt. % Alpha</u>	<u>wt. % Beta</u>	<u>wt. % Internal</u>	<u>wt. % Tri-</u>
	<u>substituted</u>			
20	89.1	0.5	1.4	0.3

The alkylation reactions were conducted at 100° C using a batch alkylation unit. The reaction time was six hours. Afterwards, the alkylated phenol was recovered by filtering and then stripping the excess phenol from
25 the product stream at 400° F and 1 torr. The recovered alkylphenol products were analyzed for monoalkyl and dialkyl content and ortho/para substitution by superfluid chromatography (SFC) and fourier transform infrared spectroscopy (FT-IR) respectively.

30 The results of the SFC analysis are set forth in the table below:

% olefin/paraffin	0.3 wt. %
% monoalkylate	86.7 wt. %
% dialkylate	12.6 wt. %
% phenol	0.1 wt. %

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The results of the FT-IR analysis for the monoalkylate are set forth in the table below:

% ortho	50.3 wt. %
% para	49.7 wt. %

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The alkylphenol was analyzed using gas chromatography and mass spectrometry. Average positional attachment results for the C₂₂ carbon are as follows:

	P ₂	P ₃	P ₄	P ₅	P ₆	P ₇	P ₈	P ₉	P ₁₀	P ₁₁
10	49.84	17.80	9.99	4.65	4.47	3.47	2.95	2.61	2.17	2.04

B. Sulfonation of Alkylated Phenols

15 The alkylated phenol was sulfonated using a falling film reactor. Reaction conditions were as follows:

Feed rate of alkylphenol was 4.26 gms/min

Charge mole ratio of sulfur trioxide to alkylphenol was 1.03:1

Air to sulfur trioxide ratio was 4:1

20

Reaction temperature was 90° C

Cyclohexamine analysis for this product indicates that a sulfonate as Ca value of 3.79 wt. % was obtained.

25 C. Neutralization

380 grams of alkylphenol sulfonic acids produced above were immediately neutralized in a stirred beaker containing 320 grams xylenes, 16 grams methanol, and 32 grams calcium hydroxide.

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D. Overbasing

450 grams of xylenes, 90 grams of methanol, and 138.5 grams of calcium hydroxide were added to a reactor and stirred for five minutes. A slurry made up of 190.0 grams of alkylhydroxy benzene sulfonic acid at 3.80 wt. % Ca as sulfonate, 160 grams xylenes, 8 grams methanol, and 16 grams calcium hydroxide, were then added to the reactor and stirred for 20 minutes. The slurry was heated to 90° F during the 20 minute stir period. 79 grams of

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carbon dioxide was charged to the reactor over 130 minutes. The rate of addition of the carbon dioxide was gradually reduced from 0.76 grams per minute to 0.25 grams per minute over the carbonation period. At 75% of the carbon dioxide charge, a second slurry made up of 190.0 grams of alkylhydroxy benzene sulfonic acid at 3.80 wt. % Ca as sulfonate, 160 grams xylenes, 8 grams methanol, and 16 grams calcium hydroxide was added. At 80% of the carbon dioxide charge, a slurry of 56 grams xylenes, 13 grams methanol, and 35.5 grams calcium hydroxide was added.

At the end of carbonation, the reactor was equipped with a condenser for stripping and the temperature was ramped to 200° F over two hours. At 200° F, the temperature was then ramped to 270° F over 30 minutes. At 270° F, 215 grams of 100 Neutral oil was added and the entire batch was then filtered through a Buchner filter. The filtrate was then stripped to 400° F at 40mm Hg vacuum. The base number was then measured with a resulting number of 318. An additional 45 grams of 100 Neutral oil was added to adjust the base number to 312.5.

The final product had a viscosity that was too viscous to measure at 100° C at a TBN of 312.5. It had 22.37% of the alkyl group of the sulfonate attached at the 4- position and higher positions of the alkyl group.

EXAMPLE 1

ALKYLATION USING ISOMERIZED OLEFINS

The procedures of the Comparative Example were repeated using a C₂₀ to C₂₄ olefin mixture isomerized by using iron pentacarbonyl isomerization. This isomerization process is known in the literature, and is disclosed in T. A. Manuel, *Journal of Organic Chemistry*, 27, 3941 (1962). The olefin mixture had the following olefinic positions, determined by using a macro program using NMR.

<u>wt. % Alpha</u>	<u>wt. % Beta</u>	<u>wt. % Internal</u>	<u>wt. % Tri-substituted</u>
0.6	13.6	97	2.4

The alkylphenol was analyzed using gas chromatography and mass spectrometry. Average positional attachment results for the C₂₂ carbon are as follows:

P ₂	P ₃	P ₄	P ₅	P ₆	- 12 - P ₇	P ₈	P ₉	P ₁₀	P ₁₁
30.23	12.52	7.92	7.57	8.05	7.05	6.74	6.18	6.61	7.11

- 5 The final product had a viscosity of 581 cSt at 100° C at a TBN of 300. It had 49.33 % of the alkyl group of the sulfonate attached at 4- position and higher positions of the alkyl group.

EXAMPLE 2**ALKYLATION USING POLYALPHA OLEFINS**

- 10 The procedures of the Comparative Example were repeated using a polyalpha olefin derived from C₁₀ dimer. The polyalpha olefin had the following olefinic positions, determined by using a macro program using NMR.

15	<u>wt. % Alpha</u>	<u>wt. % Beta</u>	<u>wt. % Internal</u>	<u>wt. % Tri-substituted</u>
	14.0	13.4	29.8	56.0

- 20 The alkylphenol was analyzed using gas chromatography and mass spectrometry. Average positional attachment results for the C₂₂ carbon are as follows:

P ₂	P ₃	P ₄	P ₅	P ₆	P ₇	P ₈	P ₉	P ₁₀	P ₁₁
48.0	16.0	7.6	7.2	5.9	5.2	4.5	3.4	2.3	0.0

- 25 The final product had a viscosity of 109 cSt at 100° C at a TBN of 296. It had 28.45 % of the alkyl group of the sulfonate attached at 4- position and higher positions of the alkyl group.

30 **COMPARISON TO COMMERCIAL METAL-CONTAINING DETERGENTS**

Results of experiments for comparing the overbased phenoxy sulfonate of the invention with commercially available metal-containing detergents are shown below

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Oxidation stability

Test method: according to JIS K-2514

Tested detergents:

Example 1: Overbased phenoxy sulfonate of invention which is

described in Example 1 of Specification

Phenate I: Commercially available overbased phenate

Phenate II: Another commercially available overbased phenate

Sulfonate: Commercially available overbased sulfonate

Salicylate I: Commercially available overbased salicylate

Salicylate II: Another commercially available overbased salicylate

Oil for test: TBN 33 in SAE #40

Test conditions: heated at 165.5°C for 72 hours

Results: set forth in the following table

15	Metal-Containing Detergent	Ratio of Viscosity (40°C)
		(Heated/Unheated)
20	Example 1	1.06
	Phenate I	1.25
	Phenate II	1.22
	Sulfonate	1.39
	Salicylate I	1.09
	Salicylate II	1.42

25 The above results show the improved oxidation stability of the phenoxy sulfonate of the invention.

Detergency at elevated temperature

Test method: Hot tube test

Oil for test: TBN 33 in SAE #40

30 Test conditions: 330°C, 16 hours

Results: set forth in the following table

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	Metal-Containing Detergent	Laquer rating (10 = Clear))
	Example 1	6.0
	Phenate I	0
	Phenate II	6.0
5	Sulfonate	0
	Salicylate I	6.0
	Salicylate II	6.0

10 The above results show the improved detergency of the phenoxy sulfonate of the invention at an elevated temperature

Thermal stability

Test method: Panel coker test

Oil for test: TBN 33 in SAE #40

15 Test conditions: 320°C, 3 hours

Results: set forth in the following table

	Metal-Containing Detergent	Deposit (mg)
	Example 1	40
20	Phenate I	10
	Phenate II	--
	Sulfonate	430
	Salicylate I	155
	Salicylate II	55

25

The above results show the improved thermal stability of the phenoxy sulfonate of the invention.

Friction Coefficient

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Oil for test:

SAE 10W30 oil is prepared by compounding a succinimide ashless dispersant, a low overbased calcium sulfonate, zinc dialkyldithiophosphate, and a viscosity index improver into 150 neutral oil. To the compounded oil is added the metal-containing detergent in an amount corresponding to TBN 10.

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Results: set forth in the following table

- 15 -

	Metal-Containing Detergent	Friction Coefficient	
		80°C	120°C
5	Example 1	0.100	0.087
	Phenate I	0.163	0.157
	Phenate II	--	--
	Sulfonate	0.137	0.132
	Salicylate I	--	--
	Salicylate II	--	--

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The above results show the reduction of friction coefficient proved by the phenoxy sulfonate of the invention.

Stability in Water

15 Test method: ASTM D-2619 (modified)

Oil for test: TBN 33 in SAE #40

Test conditions: 100 g of the test oil (its TBN is previously determined) and 5 g of distilled water are placed in a pressure-resistant bottle. The bottle is placed in an air thermostat at 93°C, for 24 hrs. under the condition that the
20 bottle is rotated with upside down at 5 r.p.m., for hydrolyzing the test oil.

The hydrolyzed test oil is then determined for its TBN. Decrease of TBN per the original TBN is calculated.

Results: set forth in the following table.

25	Metal-Containing Detergent	Decrease of TBN (%)
30	Example 1	1
	Phenate I	70
	Phenate II	20
	Sulfonate	30
	Salicylate I	1
	Salicylate II	6

The above results show the stability in water of the phenoxy sulfonate of the invention.

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EXAMPLES OF ADDITIVE PACKAGES

The following wt. % is based on the amount of an active component, namely, with neither process oil nor diluent oil. The phenoxy sulfonate employed is that described in Example 1.

I. Marine Diesel Engine Oils

10	1)	Phenoxy sulfonate	65.0 wt. %
		Primary alkyl Zn-DTP	5.9 wt. %
		Diluent oil	29.1 wt. %
15	2)	Phenoxy sulfonate	64.0 wt. %
		Alkenylsuccinimide ashless dispersant	6.3 wt. %
		Diluent oil	29.7 wt. %
20	3)	Phenoxy sulfonate	59.0 wt. %
		Primary alkyl Zn-DTP	5.4 wt. %
		Alkenylsuccinimide ashless dispersant	5.9 wt. %
		Diluent oil	29.7 wt. %
25	4)	Phenoxy sulfonate	63.6 wt. %
		Phenol type oxidation inhibitor	9.1 wt. %
		Diluent oil	27.3 wt. %
30	5)	Phenoxy sulfonate	53.5 wt. %
		Alkylated diphenylamine-type oxidation inhibitor	16.3 wt. %
		Diluent oil	30.2 wt. %
35	6)	Phenoxy sulfonate	63.6 wt. %
		Phenol-type oxidationinhibitor	4.5 wt. %
		Alkylated diphenylamine-type oxidation inhibitor	4.6 wt. %
		Diluent oil	27.3 wt. %

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5	7)	Phenoxy sulfonate	59.5 wt. %
		Primary alkyl Zn-DTP	5.4 wt. %
		Phenol-type oxidation inhibitor	5.0 wt. %
		Diluent oil	30.0 wt. %
10	8)	Phenoxy sulfonate	58.3 wt. %
		Alkenylsuccinimide ashless dispersant	5.8 wt. %
		Alkylated diphenylamine-type oxidation inhibitor	8.3 wt. %
		Diluent oil	27.5 wt. %
15	9)	Phenoxy sulfonate	57.0 wt. %
		Primary alkyl Zn-DTP	5.2 wt. %
		Alkenylsuccinic ester ashless dispersant	5.7 wt. %
		Phenol-type oxidation inhibitor	2.1 wt. %
		Alkylated diphenylamine-type oxidation inhibitor	2.0 wt. %
		Diluent oil	28.0 wt. %
20	10)	Phenoxy sulfonate	46.2 wt. %
		Overbased sulfurized alkylphenate	20.8 wt. %
		Diluent oil	44.0 wt. %
25	11)	Phenoxy sulfonate	37.0 wt. %
		Overbased sulfurized alkylsalicylate	28.0 wt. %
		Diluent oil	35.0 wt. %
30	12)	Phenoxy sulfonate	58.9 wt. %
		Overbased sulfonate	4.7 wt. %
		Primary alkyl Zn-DTP	6.5 wt. %
		Diluent oil	29.9 wt. %
35	13)	Phenoxy sulfonate	48.3 wt. %
		Overbased sulfurized alkylphenate	14.7 wt. %
		Primary alkyl Zn-DTP	6.0 wt. %
		Diluent oil	31.0 wt. %

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5	14)	Phenoxy sulfonate	40.8 wt. %
		Overbased sulfurized phenate	17.5 wt. %
		Alkenylsuccinimide ashless dispersant	6.7 wt. %
		Diluent oil	35.0 wt. %
10	15)	Phenoxy sulfonate	45.9 wt. %
		Overbased sulfurized phenate	11.5 wt. %
		Alkenylsuccinic ester ashless dispersant	4.9 wt. %
		Primary alkyl Zn-DTP	4.9 wt. %
		Diluent oil	32.8 wt. %
15	16)	Phenoxy sulfonate	63.9 wt. %
		Overbased sulfurized alkylphenate	3.3 wt. %
		Phenol type oxidation inhibitor	1.1 wt. %
		Alkylated diphenylamine-type oxidation inhibitor	1.0 wt. %
		Diluent oil	30.7 wt. %
20	17)	Phenoxy sulfonate	51.6 wt. %
		Overbased sulfurized alkylphenate	5.7 wt. %
		Primary alkyl Zn-DTP	3.3 wt. %
		Alkenylsuccinimide ashless dispersant	4.1 wt. %
		Alkylated diphenylamine-type oxidation inhibitor	1.6 wt. %
		Diluent oil	33.7 wt. %
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	18)	Phenoxy sulfonate	53.4 wt. %
		Primary alkyl Zn-DTP	3.4 wt. %
		Alkenylsuccinimide ashless dispersant	5.7 wt. %
		Demulsifier	5.7 wt. %
30		Diluent oil	31.8 wt. %
35	19)	Phenoxy sulfonate	47.0 wt. %
		Overbased sulfurized alkylphenate	16.0 wt. %
		Primary alkyl Zn-DTP	2.5 wt. %
		Alkenylsuccinimide ashless dispersant	3.4 wt. %
		Demulsifier	2.5 wt. %
		Diluent oil	28.6 wt. %

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II. Motor Car Engine Oils

5	1)	Phenoxy sulfonate	25.3 wt. %
		Alkenylsuccinimide ashless dispersant	35.9 wt. %
		Primary alkyl Zn-DTP	11.2 wt. %
		Diluent oil	27.6 wt. %
10	2)	Phenoxy sulfonate	21.1 wt. %
		Overbased sulfonate	8.6 wt. %
		Alkenylsuccinimide ashless dispersant	30.1 wt. %
		Primary alkyl Zn-DTP	9.7 wt. %
		Diluent oil	30.5 wt. %
15	3)	Phenoxy sulfonate	18.9 wt. %
		Alkenylsuccinimide ashless dispersant	39.6 wt. %
		Secondary alkyl Zn-DTP	6.3 wt. %
		Dithiocarbamate type	
		oxidation inhibitor	4.2 wt. %
		Diluent oil	31.0 wt. %
20	4)	Phenoxy sulfonate	14.9 wt. %
		Overbased sulfurized alkylphenate	3.8 wt. %
		Alkenylsuccinimide ashless dispersant	35.1 wt. %
		Secondary alkyl Zn-DTP	6.4 wt. %
		Phenol type oxidation inhibitor	4.3 wt. %
		Diluent oil	35.5 wt. %
25	5)	Phenoxy sulfonate	20.0 wt. %
		Alkenylsuccinimide ashless dispersant	32.1 wt. %
		Secondary alkyl Zn-DTP	7.1 wt. %
		Dithiocarbamate type anti-wear agent	3.6 wt. %
		Diluent oil	37.2 wt. %
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5	6)	Phenoxy sulfonate	7.4 wt. %
		Overbased sulfurized alkylphenate	8.4 wt. %
		Basic sulfonate	3.7 wt. %
		Succinimide ashless dispersant	31.6 wt. %
		Secondary alkyl Zn-DTP	5.8 wt. %
		Molybdenum-containing anti-wear agent	3.7 wt. %
		Diluent oil	39.4 wt. %
10	7)	Phenoxy sulfonate	17.7 wt. %
		Alkenylsuccinimide ashless dispersant	28.7 wt. %
		Primary alkyl Zn-DTP	3.4 wt. %
		Secondary alkyl Zn-DTP	5.0 wt. %
		Alkylated diphenylamine-type	
		oxidation inhibitor	5.7 wt. %
		Dithiocarbamate type anti-wear agent	0.9 wt. %
15		Diluent oil	38.6 wt. %
20	8)	Phenoxy sulfonate	12.9 wt. %
		Alkenylsuccinimide ashless dispersant	37.9 wt. %
		Secondary alkyl Zn-DTP	8.2 wt. %
		Phenol type oxidation inhibitor	1.0 wt. %
		Alkylated diphenylamine-type	
		oxidation inhibitor	4.1 wt. %
		Dithiocarbamate type anti-wear agent	1.0 wt. %
25		Demulsifier	0.9 wt. %
		Boron-containing friction modifier	2.1 wt. %
		Diluent	31.9 wt. %
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III. Hydraulic Oils

5	1)	Phenoxy sulfonate	4.6 wt. %
		Primary alkyl Zn-DTP	64.5 wt. %
		Phenol type oxidation inhibitor	6.6 wt. %
		Phosphorous-containing extreme pressure agent	4.9 wt. %
		Triazol type corrosion inhibitor	3.8 wt. %
10		Demulsifier	3.3 wt. %
		Nonionic anti-rust agent	3.3 wt. %
		Diluent oil	9.0 wt. %
15	2)	Phenoxy sulfonate	2.3 wt. %
		Basic sulfurized alkylphenate	2.5 wt. %
		Primary alkyl Zn-DTP	49.6 wt. %
		Phenol type oxidation inhibitor	7.3 wt. %
		Sulfur-containing extreme pressure agent	6.0 wt. %
20		Triazol type corrosion inhibitor	3.4 wt. %
		Demulsifier	5.0 wt. %
		Nonionic anti-rust agent	3.0 wt. %
25		Diluent oil	13.9 wt. %
	3)	Pehonoxy sulfonate	12.2 wt. %
		Phenol type oxidation inhibitor	14.8 wt. %
		Diphenylamine type oxidation inhibitor	7.4 wt. %
		Sulfur-containing extreme pressure agent	4.5 wt. %
30		Phosphorous-containing extreme pressure agent	39.2 wt. %
		Triazol type corrosion inhibitor	1.0 wt. %
		Demulsifier	7.0 wt. %
35		Nonionic anti-rust agent	4.5 wt. %
		Diluent oil	9.4 wt. %

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5	4)	Phenoxy sulfonate	8.5 wt. %
		Overbased salicylate	3.7 wt. %
		Phenol type oxidation inhibitor	13.5 wt. %
		Diphenylamine type	
		oxidation inhibitor	8.2 wt. %
10		Sulfur-containing extreme	
		pressure agent	4.5 wt. %
		Phosphorous-containing	
		extreme pressure agent	42.7 wt. %
		Triazol type corrosion inhibitor	1.2 wt. %
15		Demulsifier	6.5 wt. %
		Nonionic anti-rust agent	4.3 wt. %
		Diluent oil	6.9 wt. %

IV. Transmission Hydraulic Fluids

20	1)	Phenoxy sulfonate	35.9 wt. %
		Primary alkyl Zn-DTP	20.9 wt. %
		Polyol type friction modifier	17.9 wt. %
		Sulfur-containing extreme	
		pressure agent	5.8 wt. %
25		Diluent oil	19.5 wt. %
	2)	Phenoxy sulfonate	28.8 wt. %
		Basic sulfonate	11.3 wt. %
		Primary alkyl Zn-DTP	16.7 wt. %
		Amide type friction modifier	13.9 wt. %
30		Sulfur-containing extreme	
		pressure agent	6.0 wt. %
		Diluent oil	23.3 wt. %

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5	3)	Phenoxy sulfonate	32.2 wt. %
		Primary alkyl Zn-DTP	18.9 wt. %
		Alkenylsuccinimide ashless dispersant	0.5 wt. %
		Amide type friction modifier	10.4 wt. %
		Ester type friction modifier	13.9 wt. %
		Phosphorous, Sulfur-containing extreme pressure agent	6.3 wt. %
		Diluent oil	17.8 wt. %
10	4)	Phenoxy sulfonate	23.6 wt. %
		Basic sulfonate	10.1 wt. %
		Overbased salicylate	2.4 wt. %
		Primary alkyl Zn-DTP	15.2 wt. %
		Polyol type friction modifier	0.4 wt. %
15		Amide type friction modifier	8.4 wt. %
		Phosphorous, Sulfur-containing extreme pressure agent	5.1 wt. %
		Diluent oil	23.6 wt. %

20 While the present invention has been described with reference to
specific embodiments, this application is intended to cover those various
changes and substitutions that may be made by those skilled in the art
without departing from the spirit and scope of the appended claims.

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What is claimed is:

- 5 1. An additive comprising an overbased, alkyl oxy benzene sulfonate having a TBN of at least 200, wherein between 40 wt. % and 80 wt. % of the alkyl group is attached at the 4- position and higher positions of the alkyl group, and wherein the oxy is selected from the group consisting of hydroxy, methoxy, ethoxy, propoxy, butoxy, pentoxy, and hexoxy.
- 10 2. An additive according to Claim 1 wherein the overbased, alkyl oxy benzene sulfonate is produced by a process comprising:
 - (a) alkylating an oxy benzene with an olefin having between 40 wt. % and 80 wt. % internal olefins to produce an alkyl oxy benzene;
 - (b) sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid; and
 - 15 (c) overbasing the alkyl oxy benzene sulfonic acid to produce the said overbased, alkyl oxy benzene sulfonate.
- 20 3. An additive produced by a process comprising:
 - (a) isomerizing an olefin using an iron pentacarbonyl catalyst to produce an isomerized olefin;
 - (b) alkylating an oxy benzene with the isomerized olefin to produce an alkyl oxy benzene, wherein the oxy is selected from the group consisting of hydroxy, methoxy, ethoxy, propoxy, butoxy, pentoxy, and hexoxy;
 - 25 (c) sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid; and
 - (d) overbasing the alkyl oxy benzene sulfonic acid to produce an overbased, alkyl oxy benzene sulfonate having a TBN of at least
 - 30 200.
- 35 4. An additive produced by a process comprising:
 - (a) alkylating an oxy benzene, wherein the oxy is selected from the group consisting of hydroxy, methoxy, ethoxy, propoxy, butoxy, pentoxy, and hexoxy, with a polyalpha olefin having an activity of at least 80% to produce an alkyl oxy benzene;
 - (b) sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid; and

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- (c) overbasing the alkyl oxy benzene sulfonic acid to produce an overbased, alkyl oxy benzene sulfonate having a TBN of at least 200.
- 5 5. An additive according to Claim 1, 3, or 4 wherein the overbased, alkyl oxy benzene sulfonate has a TBN of at least 250.
6. An additive according to Claim 1 or 3 wherein between 45 wt.% and 70 wt. % of the alkyl group is attached at the 4- position and higher positions of the alkyl group.
- 10 7. An additive according to Claim 1, 3, or 4 wherein the oxy group is hydroxy.
- 15 8. An additive according to Claim 1, 3, or 4 wherein the alkyl group has from eighteen to thirty carbon atoms per alkyl group.
9. An additive according to Claim 8 wherein the alkyl group has from twenty to twenty-four carbon atoms per alkyl group.
- 20 10. A lubricating oil comprising:
(a) a major amount of base oil of lubricating viscosity; and
(b) a minor amount of the additive according to Claim 1, 3, or 4.
- 25 11. A lubricating oil according to Claim 10 wherein the lubricating oil is a marine lubricating oil.
12. A lubricating oil according to Claim 10 further comprising an ashless dispersant and a zinc dialkyldithiophosphate.
- 30 13. A lubricating oil according to Claim 10 further comprising a viscosity index improver.
- 35 14. A lubricating oil according to Claim 10 further comprising a detergent selected from the group consisting of metal phenates, metal sulfonates, and metal salicylates.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/16162

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10M 159/22

US CL : 252/ 18, 33

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/ 18, 33

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,523,898 (DEVAULT) 11 August 1970	1-14
A	US, A, 4,751,010 (LEONE ET AL.) 14 June 1988	1-14
X	US, A, 5,330,663 (WOLLENBERG ET AL.) 19 July 1994,	1-2, 4-10
--	col. 3, lines 24-56; col. 4, lines 24-26; col. 7, lines 6-15;	-----
Y	col. 8, lines 40-68; col. 9, lines 29-32; col. 15, lines 31-43.	1-14
Y	"LUBRICANT ADDITIVES" by SMALHEER and SMITH, 1967, pages 1-11.	12-14

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" Inter document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 MARCH 1996

Date of mailing of the international search report

20 MAR 1996

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